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GROUND STATE OF ATOMIC HELIUM

by

Wilbur Lakin

July 15, 1963

Institute of Mathematical Sciences

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- 1 -

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ABSTRACT

A variational calculation of the ground state energy is made using basis functions with the correct behavior at the simple two-electron singularities. The truncation errors obtained with few terms are not orders of magnitudes less than those obtained with a spherical harmonics expansion. It seems that the slow convergence of the Legendre expansion is not due to its inability to account for this singularity with only a finite number of terms.

Table of Contents

GROUND STATE OF ATOMIC HELIUM

1. Introduction.

There is a long history of Rayleigh-Ritz calculations of the lowest energy eigenvalue of the helium atom and isoelectronic ions.* Many contemporary studies have special purposes; one is to test trial functions with counterparts in other problems. In particular, we want to avoid trial functions with a complicated dependence upon r_{12} (the interelectronic distance), which are used in high-accuracy calculations [2,3,4]. One attempt is to avoid the use of r_{12} completely; this often leads to a Legendre expansion [5]. At first it seemed to converge rapidly, but later studies indicate a more complicated behavior [6,7,8,9]. The first few terms do indeed converge rapidly, but they converge to a value bounded from the true eigenvalue. After this the expansion converges so slowly it is useless.

This unexpected behavior of the Legendre expansion is not completely understood. It has been conjectured that this is related to the singularities of the Schroedinger equation. Specifically, the continuity properties of the derivatives of the actual Schroedinger function are different from those of the individual members of its

* For an excellent summary, see Bethe and Salpeter [1].

Legendre expansion. Consequently, the derived series must not converge uniformly, and the coefficient of the ℓ^{th} Legendre polynomial cannot decrease faster than ℓ^{-2} .* We wanted to test the conjecture by performing a Rayleigh-Ritz calculation using a trial function constructed so that a finite (small) number of terms might have the same behavior at the singularities as the solution of the Schroedinger equation. We could not do this completely; the singularity due to the coincidence of all three charges is too complicated. However it seemed worthwhile to do a more restricted calculation which takes account of the simple singularities.

At present we have only preliminary results, which are essentially negative. Our best energy eigenvalue approximately equals the F-limit, i.e. the best eigenvalue obtainable with a Legendre expansion including spherical harmonics of orders no greater than three [7]. This result indicates that either the large scale interelectron correlations cannot be represented by simple wave functions, or the complicated singularities due to coincidence of more than two charged particles is about as important as the simple ones. The first alternative is somewhat unwelcome, for although the error in the energy can easily be reduced to less than 10^{-3} times the ionization potential for atomic helium, large scale correlations are expected to be more important in many other problems.

* Schwartz [8] obtained the corresponding result for the energy.

II. General Theory.

The Schroedinger equation for a two-electron atom is

$$(2.1) \quad \left| \sum_{i=1}^2 \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{r_{12}} \right| \phi = E\phi$$

We use the usual notation; Z is the nuclear charge at the origin, r_i the radius of the i^{th} electron, and r_{12} the interelectronic distance. Equation (2.1) and the condition ϕ is in L_2 do not define an eigenvalue problem. Kato has shown there exists a self-adjoint problem such that equation (2.1) holds at its ordinary points (where no potential diverges) [10], and ϕ is everywhere continuous [11]. The local properties of ϕ follow from (2.1) and continuity alone.* When r_{12} vanishes and r_i does not vanish, the singularity is easily characterized. We introduce as new arguments of ϕ vectors r_o and r_{12} , respectively the electrons' center-of-mass and relative coordinate.

$$(2.2) \quad \left| -\frac{1}{4} \nabla_o^2 - \nabla_{12}^2 - Z \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} \right| \phi = E\phi$$

We expand ϕ formally in powers of r_{12} and substitute into (2.2) and obtain

$$(2.3) \quad \phi = a_o + a_1 r_{12} + \mathcal{O}(r_{12}^2)$$

$$(2.4) \quad -2a_1 + a_o = 0$$

* We are indebted to Prof. F. John for discussions concerning this point.

As a result of (2.4), ϕ may be written in the form

$$(2.5) \quad \phi = \phi_I + \frac{1}{2} r_{12} \phi_{II}$$

where ϕ_I and ϕ_{II} are equal if r_{12} vanishes, and are analytic* in any domain in which neither r_i vanishes.

If ω denotes the cosine of the angle between the radius vectors of the electrons, the usual Legendre expansion [5] is

$$(2.6) \quad \phi = \sum_{\ell=0}^{\infty} F_{\ell}(r_1 r_2) P_{\ell}(\omega)$$

The functions ϕ_I and ϕ_{II} may be expanded similarly. The relation between these series involves

$$(2.7) \quad r_{12} = \sum_{\ell=0}^{\infty} \left(-\frac{1}{2\ell-1} \frac{r_{\lessdot}^{\ell}}{r_{\gtrdot}^{\ell-1}} + \frac{1}{2\ell+3} \frac{r_{\lessdot}^{\ell+2}}{r_{\gtrdot}^{\ell+1}} \right) P_{\ell}(\omega)$$

Here r_{\lessdot} and r_{\gtrdot} denote respectively the lesser and greater of r_1 and r_2 . If the series for ϕ_I and ϕ_{II} converge rapidly, the expansion for ϕ must converge slowly. The crucial point is that when r_{12} vanishes, the analytic properties of the individual terms of (2.6) differ from those of ϕ itself. In contrast to this, the individual terms of (2.6) have the correct behavior when one electron is at the origin; this singularity does not affect the convergence.

We construct a trial function ϕ to approximate ϕ following (2.5)

* A function is called analytic if it is an analytic function of the six Cartesian coordinates of the individual electrons.

$$(2.8) \quad \tilde{\phi} = \tilde{\phi}_I + \frac{1}{2} r_{12} \tilde{\phi}_{II}$$

$$(2.9a) \quad \tilde{\phi}_I = \sum_{\ell} R_{I\ell}(r_1 r_2) (r_1 r_2)^{\ell} P_{\ell}(\omega)$$

$$(2.9b) \quad \tilde{\phi}_{II} = \sum_{\ell} R_{II\ell}(r_1 r_2) (r_1 r_2)^{\ell} P_{\ell}(\omega) \quad .$$

It is convenient to represent the radial functions by exponentials,

$$(2.10a) \quad R_{I\ell} = (1+P_{12}) \sum_{\nu} a_{I\ell\nu} \exp(-\kappa_{1\ell\nu} r_1 - \kappa_{2\ell\nu} r_2)$$

$$(2.10b) \quad R_{II\ell} = (1+P_{12}) \sum_{\nu} a_{II\ell\nu} \exp(-\kappa_{3\ell\nu} r_1 - \kappa_{4\ell\nu} r_2)$$

Here P_{12} is an operator which interchanges r_1 and r_2 , and a 's and κ 's with various subscripts are variational parameters.

We restrict $\tilde{\phi}$ to satisfy (2.4) as follows:

$$(2.11) \quad a_{II\ell\nu} = a_{I\ell\nu}$$

$$(2.12) \quad \kappa_{1\ell\nu} + \kappa_{2\ell\nu} = \kappa_{3\ell\nu} + \kappa_{4\ell\nu} \quad .$$

These restrictions are more stringent than needed, but conveniently give an expansion whose individual terms satisfy (2.4).

The trial energy is

$$(2.13) \quad \tilde{E} = \frac{\int \tilde{\phi} H \tilde{\phi} d^6 r}{\int \tilde{\phi}^2 d^6 r} \quad .$$

Here H is the operator on the left-hand side of (2.1) and the integration variables are the Cartesian coordinates of the

individual electrons. The formulae for all integrals needed to evaluate (2.13) are routine; the only one that might at first seem otherwise is

$$(2.14) \quad \int r_{12} \tilde{\phi}_{II} \nabla_i^2 (r_{12} \tilde{\phi}_{II}) d^6r = \int [r_{12}^2 \tilde{\phi}_{II} \nabla_i^2 \tilde{\phi}_{II} - 2\tilde{\phi}_{II}^2] d^6r .$$

An advantage of radial functions of the form (2.10) is that all integrals are the same functions of different arguments. We do not write out an explicit formula for the right-hand sides of (2.13) as it is too complicated to be illuminating.

III. Numerical Results and Discussion.

Using the IBM-7090 electronic digital computer, we evaluated \tilde{E} for atomic helium with different sets of values of the variational parameters. The values of all integrals involved were carefully checked by comparing the machine results for special cases with calculations using a desk computer. The formulae for these cases were derived independently. We believe it is very unlikely that our values of \tilde{E} for a particular set of variational parameters are incorrect. However the problem of programming the computer to search for the minimum of E proved complicated. We reached the stage where a great deal of additional work is needed to improve this part of the program significantly.* On the other hand, the partial results already obtained warrant communication.

* The difficulty of minimizing programs is that modern computers are not suited to making complex decisions. If a well understood problem like He is difficult, we must doubt results in problems not well understood.

The accuracy already obtained may be interesting since the trial functions have relatively few terms. In view of the stationary nature of E , we believe that the best values of the parameters will not reduce the errors by orders of magnitude.

If only terms with $\ell = 0$ are retained in (2.9), we have results for three terms in (2.10). We get

$$(3.1) \quad \tilde{E} = -2.89781 \quad .$$

The difference between this and our best value for only two terms in (2.10) is only 0.00030, which suggests that increasing the number of terms in (2.10) will not lead to much lower values of \tilde{E} . The above value may be compared to the S-limit [7,8]

$$(3.2) \quad E(0) = -2.87902 \quad .$$

This comparison is not illuminating because the r_{12} terms in our trial function contain considerable angular anti-correlation; this rather than the effect of the singularity probably accounts for the difference. If terms with $\ell \leq 1$ are retained in (2.9), we get

$$(3.3) \quad \tilde{E} = -2.90313 \quad .$$

This may be compared to estimated limits if terms with $\ell \leq 1$ or $\ell \leq 3$ are retained in (2.6) [7]

$$(3.4) \quad E(1) = - (2.90049 \pm 0.0001)$$

$$(3.5) \quad E(3) = - (2.90332 \pm 0.0001) \quad .$$

Despite some uncertainty in the estimated limits the value of

E as given by (3.3) is disappointing. If the value of E cannot be improved without going to very high ℓ in (2.10) we are led to the two alternatives mentioned in the introduction. Either the large-scale electron correlations give rise to the dominant errors in (3.3) and (3.5), or the complicated singularities, which arise from coincidence of more than two charges, are as important in their effects upon E as the simple ones. The second alternative is hard to believe. If the first alternative is correct, we expect that the differences between the exact* value of E and the limiting values $E(\ell)$ would continue to decrease rapidly when $\ell \geq 3$, in contradiction to the results of Schwartz [8].

We want to note a few features of our trial function $\tilde{\phi}$. Suppose we keep only the one term in (2.9), (2.10).

$$(3.6) \quad \tilde{\phi} = (1 + P_{12}) (e^{-\kappa_1 r_1 - \kappa_2 r_2} + \frac{1}{2} r_{12} e^{-\kappa_3 r_1 - \kappa_4 r_2})$$

$$(3.7) \quad \kappa_1 + \kappa_2 = \kappa_3 + \kappa_4 \quad .$$

The optimum parameters and energies are

$$(3.8) \quad \tilde{E} = -2.896665$$

$$(3.9a) \quad \kappa_1 = 2.351$$

$$(3.9b) \quad \kappa_2 = 1.374$$

$$(3.9c) \quad \kappa_3 = 1.927$$

$$(3.9d) \quad \kappa_4 = 1.798$$

* For our purposes, we assume this is -2.903724 , the six decimal approximation to Pekeris' result [4].

The eigenvalue (3.8) is good for a simple wave function. Now consider the asymptotic case $r_2 \gg r_1$

$$(3.10) \quad \tilde{\phi} \sim e^{-\chi_1 r_1 - \chi_2 r_2}$$

The correct asymptotic form is

$$(3.11) \quad \phi \sim r_2^{-0.256} \exp(-2r_1 - 1.344r_2)$$

The most striking failure of (3.10) is that the inner electron is too close to the origin. Finally, we note that our best trial function thus far, with five terms in (2.10) whose parameters are listed in table I, gives a much worse asymptotic formula

$$(3.12) \quad \tilde{\phi} \sim e^{-1.808r_1 - 0.523r_2}$$

Perhaps this indicates how little the asymptotic form affects \tilde{E} .

TABLE I

ℓ	ν	χ_1	χ_2	χ_3	χ_4	a
0	1	2.351	1.374	1.927	1.798	7.474
0	2	3.609	3.609	3.609	3.609	1.355
0	3	1.808	0.523	1.165	1.165	0.365
1	1	2.515	2.515	2.515	2.515	2.255
1	2	5.914	5.914	5.914	5.914	7.799

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